

Form PTO-1300
(Rev. 12-29-99)

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NO.

H 3391 PCT/US

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

U.S. APPLICATION NO. (known as 35 CFR 1.51)

097743465

INTERNATIONAL APPLICATION NO.
PCT/EP99/04580INTERNATIONAL FILING DATE
July 2, 1999PRIORITY DATE CLAIMED
July 10, 1998

TITLE OF INVENTION

MIXTURE OF COLOPHONIUM RESIN AND WAX

APPLICANT(S) FOR DO/EO/US

Hartmut Urbath, Johann Klein and Udo F. Windhoevel

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
 10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:**
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included
 13. ☒ A **FIRST** preliminary amendment
 - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☐ Other items or information:

"Express Mail" mailing label number: EI615774493US

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|--|--------------|---|--------------|---|-----------|
| U.S. Application No. (If known, see 37 CFR 1.46) <div style="font-size: 24pt; font-weight: bold; margin-top: 5px;">09/743465</div> | | INTERNATIONAL APPLICATION NO PCT/EP99/04580 | | ATTORNEY'S DOCKET NUMBER H 3391 PCT/US | |
| 17. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$970.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$670.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)..... \$96.00 | | | | <div style="display: flex; justify-content: space-between; font-weight: bold; font-size: 10pt;"> CALCULATIONS PTO USE ONLY </div> | |
| ENTER APPROPRIATE BASIC FEE AMOUNT | | | | = | \$ 860 |
| Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | \$ 0 | |
| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | | |
| Total Claims | 20 - 20 = | 0 | 0 X \$18.00 | \$ 0 | |
| Independent Claims | 1 - 3 = | 0 | 0 X \$78.00 | \$ 0 | |
| Multiple dependent claims (s)(if applicable) | | | 0 + \$260.00 | \$ 0 | |
| TOTAL OF ABOVE CALCULATIONS | | | | = | \$ 860 |
| Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28). | | | | \$ 0 | |
| SUBTOTAL | | | | = | \$ 860 |
| Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | \$ 0 | |
| TOTAL NATIONAL FEE | | | | = | \$ 860 |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property | | | | \$ 0 | |
| TOTAL FEES ENCLOSED | | | | = | \$ 860 |
| | | | | Amount to be: refunded: | \$----- |
| | | | | charged: | \$ 860.00 |

a. ☐ A check in the amount of \$_____ to cover the above fees is enclosed.

b. ☒ Please charge my Deposit Account No. 01-1250 in the amount of \$ 860.00 to cover the above fees.
 A triplicate copy of this sheet is enclosed. Order No. 00-0020.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 01-1250. A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b))
 must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO: Henkel Corporation, Law Dept.
 2500 Renaissance Blvd., Suite 200
 Gulph Mills, PA 19406

SIGNATURE:

 Daniel S. Ortiz
 NAME ATTORNEY FOR APPLICANT
 25,123
 REGISTRATION NUMBER

09/743465

JC07 Rec'd PCT/PTO 1 0 JAN 2001

PATENT
Docket No. H 3391 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

RE: PCT/EP99/04580
International Filing Date: July 2, 1999
Priority Date Claimed: July 10, 1998
Applicant: Urbath et al.
Title: MIXTURE OF COLOPHONIUM RESIN AND WAX
Applicants' Reference: H 3391 PCT/US

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Box PCT
Washington, DC 20231

ATTN: DO/EO/US

Sir:

Please enter the following amendments in the application after the application has been accorded a serial number and before the filing fee is calculated.

IN THE SPECIFICATION:

At page 1 place the title in all capital letters; in the line following the title, enter --FIELD OF THE INVENTION--; and after line 3 enter --BACKGROUND OF THE INVENTION--.

At page 2 after line 2, enter --BRIEF DESCRIPTION OF THE INVENTION--; and after line 19, enter --DETAILED DESCRIPTION OF THE INVENTION--.

IN THE ABSTRACT

Applicants herewith submit an ABSTRACT on a separate sheet renumbered 21 for inclusion in the application.

IN THE CLAIMS:

At page 19, delete "CLAIMS" and enter therefor --What is Claimed is:--.

Please enter the following amendments in the claims:

1. (Amended) A mixture [of] comprising at least one member selected from the group consisting of rosin and [or] rosin derivative and at least one wax, [characterized

Amendment of U.S. National Stage for International Application «EP» filed July 2, 1999

in that] wherein the waxes individually or in admixture with one another are solid at 15°C [and more particularly at 20°C].

2. (Amended) [A] The mixture as claimed in claim 1, [characterized in that] wherein at least one [the] wax[es] containing fewer C-C double bonds than corresponds to an iodine value of 100[, more particularly 75 and above all 50].

3. (Amended) [A] The mixture as claimed in claim 1, [characterized in that] wherein the waxes are solids [based on] comprising a member selected from the group consisting of linear unmodified fatty acids, modified fatty acids, [and/or] derivatized fatty acids and mixtures thereof each fatty acid containing more than 6 carbon atoms [and more particularly 8 to 22 carbon atoms].

4. (Amended) [A] The mixture as claimed in claim 3, [characterized in that] wherein the fatty acids are [obtainable] obtained by hydrogenation of fatty acids.

5. (Amended) [A] The mixture as claimed in claim 3, [characterized in that] wherein the fatty acids [were] are derivatized by esterification, amidation or reduction of the acid group[, more particularly by esterification with mono- to trihydric alcohols containing 1 to 22 carbon atoms or by amidation with ammonia, primary or secondary amines containing 1 to 22 carbon atoms].

6. (Amended) [A] The mixture as claimed in [at least one of the preceding claims, characterized in that] claim 1 comprising non-solid plasticizers [are additionally used] in quantities of 0 to 100% by weight [and preferably up to 50%,] based on the [solid] wax.

7. (Amended) [A] The mixture as claimed in claim 1, [characterized in that it] wherein the mixture has a Brookfield viscosity below 3 Pas [and more particularly below 2.5 Pas] at 70°C [where it consists of] when the mixture comprises 80% by weight of rosin and 20% by weight of waxes.

8. (Amended) [A] The mixture as claimed in [at least one of the preceding] claim[s] 1 [to 7, characterized by its composition of] comprising:

A) 5 to 50% by weight of at least one wax,

B) 95 to 50% by weight of at least one resin, based on the mixture of waxes and resins.

9. (Amended) A process for preparing the mixture claimed in [at least one of]

Amendment of U.S. National Stage for International Application «EP» filed July 2, 1999

claim[s] 1 [to 8, characterized in that] wherein the rosin and at least one solid wax, [more particularly at least one solid fatty compound,] are stirred at a temperature of at least 40°C until a transparent solution is formed.

10. (Amended) [The use of the mixture claimed in at least one of the preceding claims in the production of] An aqueous adhesive dispersion[s], [more particularly] comprising the mixture of claim 1 and [based on] a composition selected from the group consisting of [homo- or] homopolymers of acrylates containing 1 to 22 carbon atoms in an alcohol group, copolymers of acrylates containing 1 to 22 carbon atoms in [the] an alcohol group [component, more particularly with styrene or acrylonitrile] and mixture thereof.

11. (Amended) An aqueous polyacrylate-based adhesive dispersion containing the rosin and fatty compound[s according to at least one] mixture of [the preceding claims] claim 3.

12. Amended [The aqueous adhesive dispersion claimed in claim 11] A method for bonding interior floor, wall and ceiling coverings in place which comprises: applying the adhesive dispersion of claim 11 to at least on surface to be bonded and bringing the surface carrying the adhesive dispersion into contact with a second surface.

Please enter the following new claims in the application.

13. The mixture of claim 2 wherein the at least one wax has an iodine value of less than 75.

14. The mixture of claim 2 wherein the at least one wax has an iodine value of less than 50.

15. The mixture of claim 3 wherein the fatty acids contain from 8 to 22 carbon atoms.

16. The mixture of claim 3 wherein the fatty acids are derivatized by at least one method selected from the group consisting of esterification with C₁₋₂₂ alcohols containing from 1 to 3 hydroxyl groups, amidation with ammonia, amidation with a C₁₋₂₂ primary amine and amidation with a C₁₋₂₂ secondary amine.

17. The mixture of claim 7 having a Brookfield viscosity below 2.5 Pas when measured on a composition containing 80% by weight rosin and 20% by weight of wax at 70°C.

18. The mixture of claim 5 comprising: the mixture as claimed in claim 1 comprising:

A) 5 to 50% by weight of at least one wax,

**Preliminary Amendment of U.S. National Stage for International Application «EP»
filed July 2, 1999**

B) 95 to 50% by weight of at least one resin, based on the mixture of waxes and resins.
19. The mixture of claim 18 comprising non-solid plasticizers in an amount of 0-100% by weight based on the wax.
20. The mixture of claim 8 wherein the at least one wax comprises fatty acids derivitized by a method selected from the group consisting of esterification, amidation or reduction of the acid group.

DISCUSSION

Applicants request that the amendments be entered in the specification. The amendments to the specification are of a formal nature to enter headings suggested by the United States Patent and Trademark. No new matter has been entered by way of amendment to the specification.

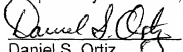
The claims have been amended to more particularly point out and clearly define what applicants consider to be their invention. The amendments to the claims are of a formal nature to place them in a form for ready examination in the United States Patent and Trademark Office.

Applicants respectfully submit that the amendments to the claims are fully supported in the specification and claims as originally filed. No new matter has been entered by the amendments to the claims.

None of the amendments to the claims have been entered to overcome any prior art reference of which applicants are aware or for any reason other than to conform them to United States claim writing practice.

Favorable consideration of the application is respectfully requested. If any additional fees are due for entry and consideration of this amendment, please charge Deposit Account No. 01-1250.

Respectfully submitted,


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JC07 Rec'd PCT/PTO 10 JAN 2001

Mixture of Colophonium Resin and Wax

This invention relates to a mixture of at least one rosin and/or a rosin derivative and at least one wax, to its production and to its use in the production of water-based adhesive dispersions.

- 5 Mixtures such as these are known. Thus, **DE 195 31 849** describes a solution of rosin in fatty acid esters. These solutions in liquid fatty acid esters are used for dispersion adhesives based on styrene/acrylate copolymers. The adhesives obtained are suitable for bonding floor coverings in place.

- 10 **WO 97/40117** relates to resin-containing dispersion adhesives based on aqueous polymer dispersions. They contain a resin preparation consisting of a mixture of 20 to 90% by weight of certain rosins and derivatives thereof and 80 to 10% by weight of oils liquid at room temperature. The liquid oils are either certain glycerol esters or certain mixtures of saturated and/or unsaturated C₁₄₋₂₂ fatty acids of vegetable
15 origin with monohydric C₁₋₁₂ alcohols.

- Although the emission levels of these dispersion adhesives containing the rosin solutions in liquid fatty acid esters are already low, a further improvement is still desirable with a view to pushing the emission levels below the odor threshold. At least the resin preparations (= mixtures
20 of rosin and/or rosin derivatives with wax) and the dispersion adhesives should be substantially odorless. In addition, the production of the dispersion adhesives, their storage and their use should of course be unchanged or even improved. This applies in particular to such an important property as initial tack in the wet state.

- 25 Accordingly, the problem addressed by the present invention was to provide a rosin mixture which would improve the production and properties of dispersion adhesives whilst at the same time avoiding all the

disadvantages mentioned, particular emphasis being placed on the substantial absence of odor and on high initial tack.

The solution is defined in the claims and consists essentially in the use of waxes solid at room temperature as carrier medium for incorporating the tackifying resins in the aqueous polymer dispersion. Accordingly, the present invention relates to a mixture of at least one rosin and/or rosin derivative and at least one wax, characterized in that the waxes individually or in admixture with one another are solid at at least 15°C and preferably at 20°C.

By "solid" is meant that the waxes, individually or in admixture, have a defined shape and offer considerable resistance to any changes therein. They do not have to be highly crystalline and, in general, are also substantially amorphous. The waxes used in accordance with the invention have a softening point (as determined by a modified ring-and-ball method, see Examples) of at least 15°C and preferably at least 20°C. They generally change into a low-viscosity state above their softening point and, in this respect, differ from resins, plastic compositions and metal soaps, etc.

Substances which are "solid" in the sense of the above definition and which also exhibit the other thermal and rheological properties are referred to as "waxes". They are generally characterized by the following properties: they are kneadable, i.e. not glass-like, at 20°C. They melt without decomposition above 40°C and become low in viscosity between 50 and 90°C. Their melt is non-stringing. They are free from ash-forming compounds.

Actual examples from the class of natural waxes are candelilla wax, carnauba wax, Japan wax, esparto grass wax, cork wax, guaruma wax, rice oil wax, sugar cane wax, ouricury wax, montan wax, beeswax, shellac wax, spermaceti, lanolin (wool wax), uropygial fat, ceresine, ozocerite (earth wax), petrolatum, paraffin waxes and microwaxes. Actual examples

from the class of chemically modified waxes include montan ester waxes, sassol waxes, hydrogenated jojoba waxes and partly oxidized polyethylene waxes. Actual examples from the class of synthetic waxes are polyalkylene waxes, polyethylene glycol waxes, ethylene/vinyl acetate waxes, acrylate waxes, ethylene/acrylic acid copolymer waxes and polybutylene glycol waxes.

Wax-like fatty compounds are preferred. The fatty compounds are linear unmodified, modified and/or derivatized fatty acids or fatty alcohols containing more than 6 and more particularly 8 to 22 carbon atoms.

Among the fatty alcohols, the relatively high molecular weight, water-insoluble fatty alcohols containing ca. 24 to 36 carbon atoms are also of interest, above all in the form of esters with relatively high molecular weight fatty acids. Examples of wax alcohols are lignoceryl alcohol [1-tetracosanol, $\text{H}_3\text{C}-(\text{CH}_2)_{22}-\text{CH}_2\text{OH}$], cetyl alcohol ($\text{H}_3\text{C}-(\text{CH}_2)_{24}-\text{CH}_2\text{OH}$), myristyl alcohol [1-triacontanol, $\text{H}_3\text{C}-(\text{CH}_2)_{28}-\text{CH}_2\text{OH}$] and melissyl alcohol [1-hentriacontanol, $\text{H}_3\text{C}-(\text{CH}_2)_{29}-\text{CH}_2\text{OH}$]. Wool wax alcohols are also understood to include triterpenoid and steroid alcohols.

Suitable fatty acids are likewise relatively high molecular weight fatty acids containing at least 22 carbon atoms, for example behenic acid, tetracosanoic acid, cerotic acid or melissic acid which - esterified with wax alcohol, steroid or triterpene alcohols - are the principal constituents of many vegetable and animal waxes.

The modification of the fatty acids is their partial or complete hydrogenation. The derivatization is an esterification, amidation or reduction of the acid group, more particularly a partial or complete esterification with mono- to trihydric alcohols containing 1 to 22 carbon atoms or a partial or complete amidation with ammonia, primary and secondary amines containing 1 to 22 carbon atoms. These derivatives are preferred to the fatty acid or the fatty alcohol or fatty alcohol ether.

The modified fatty acids may be completely or partly esterified with

alcohols. By "alcohols" are meant hydroxyl derivatives of aliphatic and alicyclic saturated, unsaturated and/or branched hydrocarbons. Both mono- and dihydric alcohols or higher alcohols are suitable. Besides monohydric alcohols, these include the low molecular weight chain extending agents or crosslinking agents containing hydroxyl groups known per se from polyurethane chemistry. Actual examples from the low molecular weight range are methanol, ethanol, propanol, butanol, pentanol, 2-ethyl hexanol, 2-octanol, ethylene glycol, propylene glycol, trimethylene glycol, tetramethylene glycol, 2,3-butylene glycol, hexamethylene diol, octamethylene diol, neopentyl glycol, 1,4-bis-hydroxymethyl cyclohexane, Guerbet alcohol, 2-methylpropane-1,3-diol, hexane-1,2,6-triol, glycerol, trimethylol propane, trimethylol ethane, pentaerythritol, sorbitol, formitol, methyl glycoside, butylene glycol, stearyl alcohol, behenyl alcohol, the reduced dimer and trimer fatty acids and higher polyethylene, polypropylene and polybutylene glycols. Monophenyl glycol or alcohols derived from rosins, such as abietyl alcohol, may also be used for the esterification. Instead of the alcohols, OH-containing tertiary amines may also be used.

Suitable "amines" for the production of amides are monoethanolamine, diethanolamine, ethylenediamine, hexamethylene diamine, ammonia, etc.

The fatty alcohols may be obtained by reduction of the acid group of the modified fatty acids or by catalytic hydrogenation of the esters of the modified fatty acids.

The fatty compounds according to the invention which emanate from the hydrogenation are partly or completely hydrogenated derivatives of unsaturated naturally occurring fatty acids, such as palmitoleic acid, oleic acid, linolenic acid, ricinoleic acid and erucic acid or mixtures of these fatty acids. Fatty compounds of this type can be obtained not only by chemical reaction, but also by physical separation processes, such as rollup

separation or freezing out, from naturally occurring fatty acid mixtures or fatty acid ester mixtures which naturally contain high levels of saturated fatty acids such as, for example, animal fats or palm oil. Examples include palmitic acid, palmitic acid methyl ester, palmitic acid triglyceride, palmitoyl alcohol, palmitic acid monoethanolamide, elaidic acid, elaidic acid methyl ester, stearic acid, stearic acid methyl ester, stearyl alcohol, stearic acid aryl ester, 12-hydroxystearic acid methyl ester, 12-hydroxystearyl alcohol, hydrogenated castor oil, behenic acid methyl ester.

The modified fatty compounds may be produced either from the modified fatty acids or by modification of corresponding fatty compounds.

Commercially available technical mixtures which, besides the modified fatty compounds described above, contain other secondary constituents known to the expert, such as short-chain, non-linear, branched fatty acids containing functional groups, are normally used. The secondary constituents are partly unknown and may make up as much as 50% by weight, depending on the particular modification and the starting material.

The modified fatty compounds may be both vegetable and animal in origin.

The following products of Henkel KGaA are mentioned as examples: Edenor ME ST 1 (stearic acid/palmitic acid mixture), Edenor FHTi (stearic acid, technical), Edenor C 16 92-94 (palmitic acid), Edenor C 18 98-100 (stearic acid), Edenor C 22 85 R (behenic acid), Edenor ME AS 16 (palmitic acid methyl ester), Edenor Me Ti (stearic acid methyl ester, technical), Lorol C 18 (stearyl alcohol), Stenol 1822 A (behenyl alcohol), Stenol 16-18 (palmityl/stearyl alcohol), Edenor NHTi (stearic acid triglyceride).

The following products of Unichema are mentioned as examples: Uniwax 1750 (stearic acid amide), Uniwax 1760 (ethylene-bis-stearamide), Estol 1482 (methyl stearate), Estol CEP (cetyl palmitate), Estol MEP (methyl palmitate), Prifac 5902 (partly hydrogenated tallow fatty acid), Prifac 2981 (stearic acid) and Pristerene 4913 (palmitic/stearic acid

triglyceride).

Mixtures of Pristerene 4913 and Priolube 1451 and of Edenor FHTi and Estol CEP are mentioned as example of mixtures of commercially available products.

- 5 The fatty compounds are substantially saturated or contain trans-double bonds: they contain C-C double bonds in a concentration corresponding to an iodine value of less than 100, more particularly less than 75 and above all less than 50.

- 10 In order to improve the adhesive properties and/or the rheology of the adhesives, up to 100% and preferably up to 50%, based on the solid wax and depending on the type of polymers used, of plasticizers that do not correspond to the invention, as described for example in **WO 96/06897**, may also be used. Examples of such plasticizers are liquid fatty acid esters, such as methyl laurate, isopropyl myristate, octyl caprylate, 15 epoxidized fatty compounds, such as epoxidized soybean oil, epoxidized linseed oil, epoxystearic acid methyl ester, diepoxystearic acid methyl ester, epoxystearic acid-2-ethyl hexyl ester, vernonia oil, epoxidized palm kernel oil, esters of glycerol such as, for example, triacetin, caprylic/capric acid triglyceride, rapeseed oil, soybean oil and castor oil. However, 20 standard petrochemical-based plasticizers known to the expert, such as phthalic acid esters, monophenyl glycol, adipic acid esters, chloroparaffins, polymeric plasticizers, benzoic acid esters, trimellitic acid esters and citric acid esters, may also be used.

- 25 The liquid plasticizers additionally used may be added both to the resin melt and - preferably - to the final adhesive formulation.

However, it is important that the mixture of wax and additional plasticizer also have a softening point of at least 15°C and preferably at least 20°C.

- 30 Rosin is the generic name for gum, wood and tall-oil rosins. These rosins are resins of vegetable origin which exist as complex mixtures of so-

called resin acids. Such natural resin acid mixtures consist essentially of special unsaturated carboxylic acids with the empirical formula $C_{20}H_{30}O_2$, for example abietic acid, neoabietic acid, levopimaric acid, pimaric acid, isopimaric acid, palustric acid etc., optionally with small amounts of

5 hydrogenated, dehydrogenated or oxidized resin acids and so-called neutral substances, such as fatty acid esters, terpenes, terpene alcohols and hydrocarbons.

Besides the rosin itself, chemically modified rosins with a softening range or melting point of 15 to 130°C are also suitable as tackifying resins.

10 These modified rosins are in particular rosin derivatives obtained by isomerization, dimerization, polymerization, disproportionation or hydrogenation and/or by homogeneous or mixed esterification with mono-, di- or polyhydric alcohols, for example with methanol, ethylene glycol, diethylene glycol, triethylene glycol, glycerol, pentaerythritol etc., and by

15 esterification of resin acid derivatives such as, for example, esters of hydroabietyl alcohol with mono- or polyhydric alcohols. Paraformaldehyde-modified rosins may also be used.

The rosin or its derivative preferably has a softening range of 15 to 130°C and more particularly 15 to 95°C (ring-and-ball). Preferred resins

20 are liquids of medium to high viscosity at room temperature or solids melting at temperatures of up to 120°C.

High initial tack and cohesion of the dispersion adhesives produced in accordance with the invention can be achieved above all with resin preparations of resins which are themselves solid and have a melting point

25 or softening range of 50 to 130°C. Resin preparations of resins which are themselves liquid or have a melting point or softening point of 25 to 50°C give softer dispersion adhesives with good initial tack but relatively poor cohesion. According to the invention, resin preparations with which the tack and strength properties of the dispersion adhesives produced from

30 them can be adjusted as required can be produced by selecting suitable

resins or by mixing resins with different melting points or softening ranges.

Other tackifiers, above all hydrocarbon or phenolic resins or terpene/phenol resins, may be used instead of or preferably in addition to the rosins. These resins may be used either individually or in the form of mixtures; they are preferably used in a percentage by weight of 0 to 80% by weight and more particularly 5 to 40% by weight in addition to the rosins.

Any reference to "resins" in the following is meant to apply to at least one of the resins described above.

According to the teaching of the present invention, resin preparations in which the resin to wax ratio is as high as possible and which have a viscosity at 20 to 100°C that still just allows them to be handled, pumped and mixed lead to a higher initial tack and cohesion - for the same percentage content in the dispersion adhesives produced from them - than resin preparations with a relatively low resin-to-wax ratio. Relatively low resin-to-wax ratios lead to resin preparations with a lower viscosity and give softer dispersion adhesives with lower initial tack and cohesion, but with a longer open time. Basically, compositions of 5 to 50% by weight, more particularly 10 to 20% by weight of at least one wax and 95 to 50% by weight, more particularly 80 to 90% by weight of at least one resin, based on the mixture of waxes and resins, are suitable. The most suitable resin-to-wax ratios depend upon the nature of the resins and waxes, upon the required viscosity of the resin preparation and upon the required properties of the dispersion adhesive. They may readily be determined by tests.

The mixture according to the invention may also contain auxiliaries, for example to reduce the viscosity of the resin solution or to improve its compatibility with the polymer dispersion.

According to the teaching of the invention, the initial tack and cohesion attainable in a dispersion adhesive increase with the amount of resin preparation incorporated for the same resin-to-wax ratio providing the

resin preparation is selected from those of which the inherent tack and inherent cohesion exceed those of the adhesive preparation to which the resin preparation has not been added. Quantities of the resin preparation in the dispersion adhesive of 5 to 60% are suitable for the purposes of the invention, quantities of 10 to 25% being preferred.

The resin preparations according to the invention (= mixture of resin and wax) are produced by introducing the wax into a heatable mixing vessel and heating it to a temperature of at least 40°C and preferably in the range from 60 to 120°C. The resins are added in portions with stirring and mixed in until a transparent mixture is formed. The resulting preparation may then be heated with stirring for about 30 minutes to several hours to a temperature of around 100°C in order to remove volatile ingredients, for example terpenes, from the rosins, optionally via a condenser. The solid wax is preferably introduced into a heatable mixing vessel together with the resin, heated to 60 to 90°C and stirred until a transparent mixture is formed.

The mixed homogeneous resin preparation is preferably heated or cooled with stirring to a temperature of 20 to 95°C and preferably to a temperature of 75 to 85°C and is then immediately processed at temperatures in that range or stored. The liquid resin preparation may therefore be directly added to and mixed with the polymer dispersion or mixture of the other adhesive constituents introduced into another mixer. However, it may also be cooled and reheated before dispersion or stored at a temperature at which it remains liquid and pumpable.

The resin preparation according to the invention is preferably a homogeneous mixture which is reflected in its transparency.

The resin preparations according to the invention satisfy the requirements made of them to a large degree within the quantity ranges according to the invention. They are homogeneously liquid and can be adjusted to the viscosity required for handling at a temperature of 20 to

95°C. The resin preparations according to the invention may readily be incorporated in dispersion preparations and surprisingly provide the dispersion adhesives produced with them with initial tacks that can be varied within wide limits. There is no evidence of any adverse effect on the floor coverings bonded in place with the dispersion adhesives.

The liquid carrier media used in accordance with the invention do not have a measurable vapor pressure so that the VOC emissions of the resin preparation are largely confined to the emissions of the resins used. The dispersion adhesives produced therewith have a distinctly weaker odor than adhesives produced by known methods both in the early phase and in the long-term phase. Accordingly, they meet the requirements of an integrated safety-at-work, environmental and consumer protection policy to a high degree. By virtue of their increased percentage of renewable biodegradable constituents, they are also environmentally compatible to an increased extent.

The resin preparation according to the invention is distinguished by a low viscosity at 70°C. It is below 3 Pas and preferably below 2.5 Pas for a mixture of 80% by weight rosin and 20% by weight wax (Brookfield BT, spindle 4, 20 r.p.m.). This surprising effect may be utilised in different ways, for example to increase the resin concentration or to lower the processing temperature. It also has an effect on the rheology of the adhesive: the dispersion is easier to spread.

The resin preparations according to the invention may be used for the production of resin-containing polymer dispersions or resin-containing aqueous dispersion adhesive. Polymer dispersions known per se with adequate shear stability at 20 to 70°C, for example aqueous dispersions of homo-, co- and above all block copolymers based on acrylates, methacrylates, acrylic acid, methacrylic acid, acrylonitrile, vinyl acetate, vinyl chloride, ethylene, styrene, butadiene, etc. and mixtures of such polymer dispersions, have proved to be suitable for this purpose. This list

is intended purely as an example: the basic suitability of other polymer dispersions may be established by simple laboratory tests. Homopolymers and copolymers of vinyl acetate, more particularly with ethylene, and homopolymers and copolymers of acrylates containing 1 to 22 carbon atoms in the alcohol component, more particularly with styrene or acrylonitrile, are preferred.

The resin preparations according to the invention may be incorporated in dispersion adhesives by various methods known to the expert as already hitherto practised with known resin preparations. In the most simple case, the polymer dispersion - optionally containing dispersants and defoamers and other additives and fillers - is introduced first and the liquid resin preparation is dispersed therein in portions. Both the dispersion preparation introduced first and the resin preparation may have a temperature of 20 to 95°C and preferably a temperature of 50 to 85°C during the dispersion process. The optimum incorporation temperatures are dependent on the temperature stability of the dispersion preparation and the viscosity of the resin preparation. Dispersion is continued until a homogeneous resin preparation is present. The expert on dispersion adhesives is familiar with this procedure.

In a preferred embodiment, the still resin-free dispersion preparation is introduced into a heatable mixing vessel and heated to a temperature of 20 to 95°C. The liquid resin preparation is then added with stirring at a temperature of 20 to 95°C and incorporated by dispersion until a homogeneous resin preparation is obtained.

The dispersion adhesives according to the invention preferably consist of:

- a) 5 to 60% by weight of the resin preparation according to the invention and
- b) 40 to 95% by weight of aqueous polymer dispersions and emulsions known per se optionally containing additional dispersants, defoamers,

preservatives, thickeners, anti-flow agents, additives and fillers known per se.

- 5 Aqueous adhesive dispersions based on polyacrylates containing the preparation according to the invention of rosin and fatty compounds are particularly preferred. They are particularly suitable for bonding interior floor coverings, wall coverings and ceiling coverings.

The adhesives according to the invention are distinguished by high wet bond strength, good spreadability, minimal emission and above all by the substantial absence of odor.

10

Examples

I. Determination of the softening points of the waxes or wax mixtures

| Components | % by weight | Softening point (°C) |
|---|-------------|----------------------|
| Palmitic/stearic acid methyl ester (ca. 50:50) techn. | 100 | 27.1 |
| Palmitic/stearic acid methyl ester (ca. 50:50) techn. | 90 | 25.5 |
| Epoxidized fatty acid methyl ester | 10 | |
| Palmitic/stearic acid methyl ester (ca. 50:50) techn. | 70 | 22.3 |
| Epoxidized fatty acid methyl ester | 30 | |
| Palmitic/stearic acid methyl ester (ca. 50:50) techn. | 70 | 21.5 |
| Dibutyl phthalate | 30 | |
| Palmitic/stearic acid methyl ester (ca. 50:50) techn. | 70 | 21.4 |
| Rapeseed oil methyl ester | 30 | |
| Stearyl alcohol | 100 | 57.0 |
| Stearyl alcohol | 70 | 52.5 |
| Epoxidized fatty acid methyl ester | 30 | |
| Stearyl alcohol | 50 | 50.3 |
| Epoxidized fatty acid methyl ester | 50 | |

| | | |
|---------------------------------------|-----|------|
| Hydrogenated bovine tallow | 100 | 50.0 |
| Hydrogenated bovine tallow | 33 | 43.5 |
| Diocetyl adipate | 77 | |
| Beeswax | 100 | 62.6 |
| Polyethylene glycol | 100 | 51.6 |
| Carnauba wax | 100 | 80.5 |
| Myristic acid | 50 | 48.9 |
| Epoxidized soybean oil | 50 | |
| Myristic acid | 100 | 53.3 |
| Beeswax | 75 | 58.9 |
| Sunflower oil fatty acid methyl ester | 25 | |
| Paraffin wax | 100 | 59.3 |
| Paraffin wax | 50 | 52.8 |
| Diocetyl adipate | 50 | |
| Paraffin wax | 30 | 47.8 |
| Rapeseed oil methyl ester | 70 | |
| Polyethylene wax | 50 | 48.3 |
| Epoxidized fatty acid methyl ester | 50 | |
| Carnauba wax | 70 | 76.7 |
| Diocetyl adipate | 30 | |
| Carnauba wax | 70 | 77.8 |
| Epoxidized fatty acid methyl ester | 30 | |

II. Production and properties of the resin solutions

The resin solution was prepared in a heatable stirred tank. To this end, resin and fatty acid ester were introduced in the ratio by weight shown and stirred at a temperature of 80°C until a transparent solution was obtained (ca. 1.5 h).

Resin solution 1: 80% gum rosin

- (RS 1) 20% myristic acid methyl ester
 Resin solution 2: 80% gum rosin
 (RS 2) 20% tall oil fatty acid butyl ester
 Resin solution 3: 80% gum rosin
 (RS 3) 20% palmitic/stearic acid methyl ester (in a ratio by weight of ca. 50:50)

Table II. Properties of the resin solution

| | RS 1 | RS 2 | RS 3 |
|------------------|-------|-------|-------|
| Viscosity (mPas) | 2,900 | 3,100 | 1,200 |
| Odor | 3.5 | 4.5 | 3.5 |

Remarks:

The properties were determined as follows:

1. Viscosity measurement: Brookfield HBT, spindle 4, 20 r.p.m., 70°C
2. Odor test: Ca. 50 g of resin solution were poured into a 250 ml screw-top glass flask which was then closed and stored for 3 days at 23°C. At least 5 volunteers then evaluated the odor on the following scale: 1 odorless, 2 perceptible, 3 tolerable, 4 troublesome, 5 intolerable.

III. Use of the resin solutions for the production of adhesives

The resin solutions heated to around 80°C were added over a period of 30 minutes with vigorous stirring at 20°C to an aqueous dispersion with the following composition (in % by weight):

| | Adhesives 1-3 | Adhesive 4 |
|-------------------------------|---------------|------------|
| Acrylate copolymer dispersion | 25 | 25 |
| Dispersion aids/emulsifiers | 2 | 2 |

| | | |
|------------------------------------|-----|-----|
| Preservative | 0.1 | 0.1 |
| Defoamer | 0.1 | 0.5 |
| Filler (CaCO ₃) | 50 | 49 |
| Resin solution | 17 | 17 |
| Water | 5.3 | 5.3 |
| Epoxidized fatty acid methyl ester | 0 | 1 |

The acrylate copolymer dispersion is a commercially available 60% aqueous dispersion of a copolymer of - mostly - butyl acrylate and less than 15% of acrylonitrile (a product of BASF). The adhesives were tested, the test results being set out in Table III.

Table III. Adhesive properties

| | Adhesive 1 with RS 1 | Adhesive 2 with RS 2 | Adhesive 3 with RS 3 | Adhesive 4 with RS 4 |
|--|-------------------------|-------------------------|-------------------------|-------------------------|
| Viscosity [Pas] | 21.9 | 20.7 | 21.5 | 20.9 |
| Wet bond strength [N/cm] | | | | |
| after 10 mins. airing | 5.0 | 6.25 | 7.5 | 6.5 |
| after 15 mins. airing | 5.5 | 6.25 | 7.5 | 6.5 |
| after 20 mins. airing | 3.5 | 6.25 | 8.8 | 7.0 |
| Open time [mins] | 15 | 25 | 25 | 25 |
| Odor: | | | | |
| adhesive, wet | 3.2 | 4.0 | 3.2 | 3.2 |
| adhesive, dry | 2.8 | 4.0 | 2.5 | 2.4 |
| Pollution of indoor air [$\mu\text{g}/\text{m}^3$] | > 600 | < 300 | < 300 | < 300 |

Remarks:

The tests were carried out as follows:

1. Viscosity:

Brookfield HBT, spindle 4, 20 r.p.m., 23°C

2. Wet bond strength:

The adhesive is applied (ca. 350 g/m²) with a toothed spatula to a chipboard coated with a cement-based surfacing compound. After different airing times, 5 cm wide strips of a carpet with a fabric backing were placed on the bed of adhesive and rubbed in. After 5 minutes, the strips were removed vertically at a rate of 1 cm/sec. and the removal force was determined with a spring balance.

3. Open time.

The open time is the maximum period for which an adhesive may be left to air. The end of the open time is reached when the back of a foam-backed strip of a textile covering is less than 30% wetted.

4. Odor wet:

See odor test, resin solution.

5. Odor dry:

A ca. 200 µm thick film of adhesive is knife-coated onto a glass plate (5 x 10 cm) and dried for 24 h at 23°C/50% relative humidity. The glass plate is then transferred to a 500 ml screw-top glass flask and stored for 3 days at 23°C. The odor is evaluated in the same way as for the resin solutions.

6. Pollution of indoor air:

The expected pollution of indoor air is determined in a model test chamber. To this end, 300 g/m² adhesive is applied to a glass plate using a toothed spatula and placed in a test chamber. After 10 days' storage under the following conditions: 23°C, 50% rel. humidity, 0.5 air changes per hour and 0.4 m² sample per m³ air space, a sample of the air is analyzed for volatile organic compounds. The results are expressed as the TVOC content (= total volatile organic compounds) in µg/m³.

7. Iodine value:

The Kaufmann iodine value is determined by DGF method C-V 11b.
The Wijs iodine value is determined by DGF method C-V 11 d (ISO 3961).

8. Transparency:

- 5 The mixture is poured into a Petri dish and visually assessed at room temperature in a layer thickness of 5 mm: it must be clear in appearance with no streaks or fatty globules.

9. Softening points:

- 10 Method (modified ring-and-ball): 20 ml of the wax or wax mixture are poured into a 25 ml glass beaker (diameter 30 mm, height 48 mm) and cooled to ca. 10°C in an ice bath. A cold steel ball (weight 32.2 g, diameter 19 mm) is placed on the solid mixture which is then slowly heated. The softening point is defined as the temperature at which the steel ball begins to sink to the bottom.

15 IV. Results

- The results show that the resin solution according to the invention (RS 3) and a dispersion adhesive produced therewith for floor coverings is at least comparable in performance with known adhesives and, in addition,
20 is substantially free from odor. If a liquid plasticizer, for example an epoxidized fatty acid methyl ester, is also added, there is a distinct improvement in wet bond strength with no adverse effect on odor or VOC content.

- A comparable improvement in wet bond strength can also be
25 achieved by addition of non-epoxidized fatty acid esters, for example palmitic acid methyl ester. However, the cohesion of the adhesive is seriously impaired, as can easily be demonstrated by shear tests. To the user of the adhesive, this means that difficult floor coverings cannot be bonded with such a soft adhesive. The use of epoxidized fatty acid esters,
30 more particularly epoxy stearic acid methyl ester, surprisingly does not

- affect the cohesion of the adhesive. Epoxidized fatty acid esters are compatible with gum rosin and non-epoxidized fatty acid esters and, accordingly, may also be directly added to the resin mixture in quantities of up to 15% and preferably up to 6% instead of non-epoxidized fatty acid esters. This simplifies production of the adhesive.
- 5

CLAIMS

1. A mixture of at least one rosin and/or rosin derivative and at least one wax, characterized in that the waxes individually or in admixture with one another are solid at 15°C and more particularly at 20°C
- 5 2. A mixture as claimed in claim 1, characterized in that the waxes contain fewer C-C double bonds than corresponds to an iodine value of 100, more particularly 75 and above all 50.
3. A mixture as claimed in claim 1, characterized in that the waxes are solids based on linear unmodified, modified and/or derivatized fatty acids
- 10 containing more than 6 carbon atoms and more particularly 8 to 22 carbon atoms.
4. A mixture as claimed in claim 3, characterized in that the fatty acids are obtainable by hydrogenation of fatty acids.
5. A mixture as claimed in claim 3, characterized in that the fatty acids
- 15 were derivatized by esterification, amidation or reduction of the acid group, more particularly by esterification with mono- to trihydric alcohols containing 1 to 22 carbon atoms or by amidation with ammonia, primary or secondary amines containing 1 to 22 carbon atoms.
6. A mixture as claimed in at least one of the preceding claims,
- 20 characterized in that non-solid plasticizers are additionally used in quantities of 0 to 100% and preferably up to 50%, based on the solid wax.
7. A mixture as claimed in claim 1, characterized in that it has a Brookfield viscosity below 3 Pas and more particularly below 2.5 Pas at 70°C where it consists of 80% by weight of rosin and 20% by weight of
- 25 waxes.
8. A mixture as claimed in at least one of the preceding claims 1 to 7, characterized by its composition of
 - A) 5 to 50% by weight of at least one wax,
 - B) 95 to 50% by weight of at least one resin, based on the mixture of
- 30 waxes and resins.

9. A process for preparing the mixture claimed in at least one of claims 1 to 8, characterized in that the rosin and at least one solid wax, more particularly at least one solid fatty compound, are stirred at at least 40°C until a transparent solution is formed.
- 5 10. The use of the mixture claimed in at least one of the preceding claims in the production of aqueous adhesive dispersions, more particularly based on homo- or copolymers of acrylates containing 1 to 22 carbon atoms in the alcohol component, more particularly with styrene or acrylonitrile.
- 10 11. An aqueous polyacrylate-based adhesive dispersion containing rosin and fatty compounds according to at least one of the preceding claims.
12. The aqueous adhesive dispersion claimed in claim 11 for bonding interior floor, wall and ceiling coverings in place.

ABSTRACT

A mixture of colophonium resins and their derivatives with a wax which is solid at 15°C. the waxes are wax-type fatty composition based on fatty acids having more than 6 carbon atoms. The mixture is useful for preparing low-emission aqueous adhesive dispersions having low odor. The adhesive dispersions are particularly useful as adhesives for floor, wall and ceiling coverings.

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket
Number

H 3391 PCT/US

First Named
Inventor

Urbath, Hartmut

COMPLETE IF KNOWN

Application Number

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

MIXTURE OF COLOPHONIUM RESIN AND WAX

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY)

7/2/1999

as United States Application Number or PCT International

Application Number

PCT/EP99/04580

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §385(b) of any foreign application(s) for patent or inventor's certificate, or §385(e) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY) | Priority Not Claimed | | Certified Copy Attached? | |
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DECLARATION

Page 2

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| U.S. Parent Application Number | PCT Parent Number | Parent Filing Date (MM/DD/YYYY) | Parent Patent Number (if applicable) |
|--------------------------------|-------------------|---------------------------------|--------------------------------------|
| | PCT/EP99/04580 | 7/2/1999 | |

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:

☐ A petition has been filed for this unsigned inventor

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| DECLARATION | | | | ADDITIONAL INVENTOR(S) Supplemental Sheet | | | |
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